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Gas phase oxidation of benzene to phenol using Pd-Cu composite catalysts. Effect of temperature, feeding gas and catalyst composition

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Catalytic oxidation of benzene in the gas phase has been studied as a function of the catalyst composition, reaction temperature and the feed conditions of reactant gases, hydrogen, oxygen, benzene as well as diluting inert gas. The catalyst tested is composed of Pd and Cu(I) ions, both of which are supported on silica gel. If one of the two metal species is lacked from the catalyst, no catalytic activity appears. The product is almost exclusively phenol and some accompanying benzoquinone, in particular at lower temperatures, as minor byproduct.

Keywords: Oxidation; benzene; phenol; Cu-Pd catalyst

1. Introduction

We have reported in several previous papers [1–4,7,8] that phenolic compounds can readily be obtained from benzene by using the Cu(I)/Cu(II) redox couple as the charge transfer catalyst. We have further shown that the charge transfer cycle works efficiently by either electrolytic reduction of Cu(II) ion [1,2] or by using heterogeneous catalyst based on palladium supported on silica [3,4]. Of these, the electrolytic method, if it is conducted in aqueous solutions, favors the production of quinones but, when phenol is the desired product, the use of a heterogeneous catalyst is much advantageous.

Recently, an improvement in the electrolysis technique was reported by Ohtsuka and his colleagues [5,6]. Their method seems to provide a possibility for applying the electrolytic method to the phenol producing process.

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In the previous papers, our interests were restricted in the reactions occurring in the liquid phase. The reaction in the liquid phase, however, has some limitations, particularly for the reaction of solid materials such as naphthalene, anthracene and others. In order to be free from this limitation, we have studied the possibility of doing the reaction in the gas phase. The model reaction employed here is still of benzene, however.

2. Experiments

REACTOR

The reactor used is shown schematically in fig. 1. All parts of it were made of Pyrex glass. The catalyst, normally 1 or 2 grams, was placed over the sintered glass plate located half way the vertically hold reactor tube, which was surrounded by an electric furnace. Except for some preliminary experiments the temperature was monitored inside the catalyst layer.

To the lower end of the tube, a 50 ml round bottom flask was attached. In experiments of an early stage, a given amount of benzene was put into the flask and a stream of reacting gases was introduced so as to sweep the surface of benzene and to carry it together to the reactor. In this case, the flask temperature was maintained at slightly below the boiling point of benzene (70°C). In later experiments, the flask was replaced by a flush evaporator (ca. 20 ml) and a liquid stream of benzene at a controlled rate was introduced to its heated wall (140°C). Hydrogen and oxygen were supplied in the same manner as above. The outgoing gas stream from the reactor was bubbled into ethanol in the exit trap, which is located near the top of the reactor tube, before releasing it into the atmosphere. In this way, most of the products were captured in the ethanol trap. An appreciable amount of unreacted benzene also condenses at the trap but a considerable part of it revaporizes into the exhaust gas. Products trapped in ethanol were directly analyzed with HPLC.

CATALYST

The catalyst was prepared by depositing both $CuSO_4$ and $PdCl_2$ on a given amount of silica gel (Merck Kiesel Gel 60). They are denoted in this paper as xCu-yPd, where x and y stand for number of micromoles of metal species per gram of the silica support.

As will be shown later, an appreciable amount of phenolic products is captured, particularly at lower temperatures, in the catalyst layer as well as on the reactor wall. We shall call this “hold-up” in the following description. In order to determine the amount of the hold-up, catalyst and inner wall of the reactor tube were washed with a given amount of ethanol.

For safety caution to hazardous explosion, the size of the catalyst was

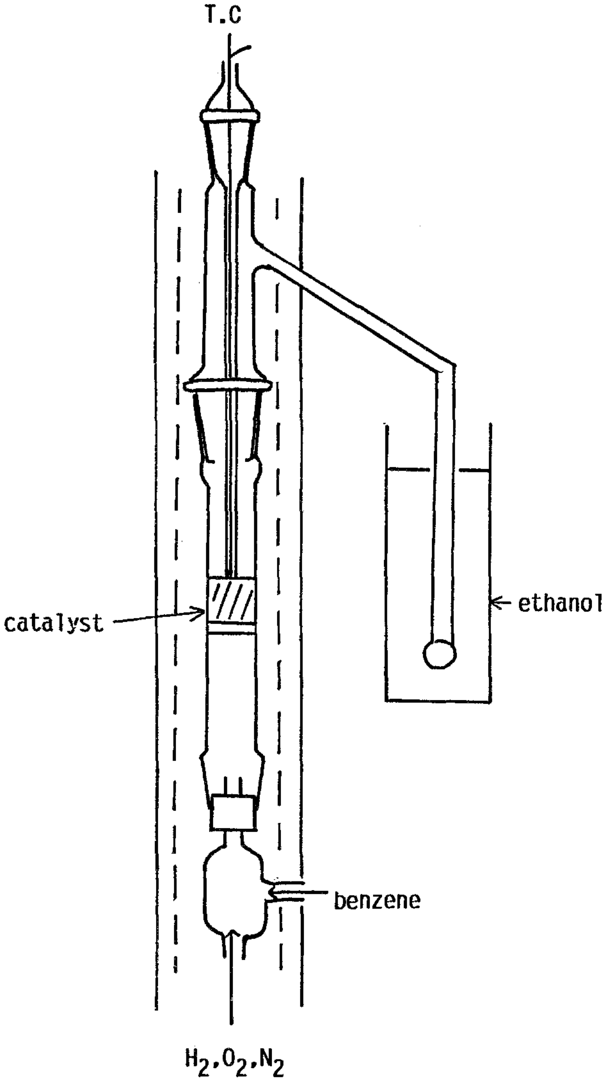

Fig. 1. Schematic view of the reactor.

minimized and the reactor tube was covered by a double cylinder of stainless steel mesh although no explosion has been encountered yet.

3. Results

During the stage of preliminary experiments, the reaction was carried out at a temperature of ca. 80°C. Four catalysts with different composition (50Pd, 62.5Cu-50Pd, 250Cu-50Pd, and 1000Cu-50Pd) were used. In this experiment, the

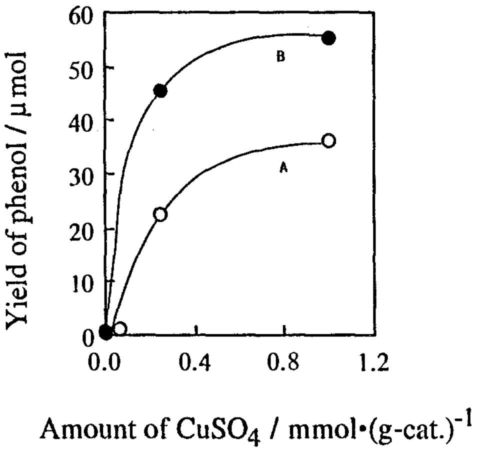

Fig. 2. Yield of phenol as a function of copper content in the catalyst and the effect of the mode of gas supply. A: Air (25 ml/min) was supplied to preliminarily activated catalysts. B: Both hydrogen and air were supplied simultaneously (20 ml/min for each). Catalyst: variable *x*-50 Pd, 2 g.

temperature was monitored only at the outer wall of the reactor tube and thus the real temperature inside the catalyst layer would be lower because of the continuous gas flow. Fig. 2 shows the results obtained. Phenol yield after 2 hr of reaction is plotted as a function of the catalyst composition. For obtaining curve A, the air in the reactor tube was first replaced by a stream of nitrogen which was then followed by a hydrogen stream (50 ml/min) to activate the catalyst for one hour. After this, the hydrogen was replaced by an air stream (25 ml/min) and the reaction was continued for 2 hours.

In contrast, curve B was obtained by feeding both hydrogen and air (20 ml/min for each) simultaneously for 2 hours. Both the experiments indicate that, irrespective of the mode of gas supply, the phenol yield increases with increasing amount of copper in the catalyst. With the Pd-alone catalyst, the yield of phenol is very little (only 2% of the yield with 1000Cu-50Pd). This is in marked contrast to a similar reaction occurring in the liquid phase [4,7,8], in which the Pd-alone catalyst gives the highest yield of phenolic products. The yield of the byproduct, benzoquinone, is also suppressed in the gas phase reaction. At lower temperatures, benzoquinone is detected by an amount of several percent of the total yield of phenol. The yield decreases with increasing reaction temperature and when the temperature exceeds 150°C the selectivity of phenol amounts to more than 98%. Accordingly, the yield of benzoquinone is ignored in the following part of this report.

In the above experiments, most of the products were detected in the catalyst layer and only a few were flown out to the trap. We thus tried to raise the reaction temperature. Hereafter, the mode of the gas supply was fixed to simultaneous feeding. In addition, the temperature of the catalyst itself was made to be monitored.

1. EFFECT OF TEMPERATURE

The effect of the temperature was studied using the 125Cu-25Pd catalyst. The yield of phenol first increased with increasing temperature up to 150°C or so and, above that, it became almost constant at a value of $45 + 10$ μmol/(hr,g-cata). At temperatures exceeding 350°C it seemed to decrease. The reason why the maximum rate is attained at 150°C is not certain. The fact that hydrogen peroxide decomposes at its boiling point (151°C) may have some correlation. The effect of the temperature, particularly at temperatures higher than 150°C, seems to require some further studies in correlation with other reaction conditions such as the nature of catalyst, gas composition, etc. An important thing to be noted is the amount of hold-up of the products in the catalyst layer. The hold-up is of course expected to increase with the decrease in both temperature and flow rate of the reactant gases. In fact, when the reactor temperature was 100°C, an appreciable part of the products (ca. 75%) was still not flown out to the exit trap but remained in the catalyst layer while at 160°C, slightly lower than the boiling point of phenol, most of phenol was entrained with the streaming gases and was captured in the exit trap.

Of course, the percentage hold-up is thought to be a function of various factors such as the length of reaction time, flow velocity of the gases, and length of the catalyst bed. Accordingly, when the reaction is continued for longer times to attain a steady state the percentage of hold-up will decrease.

2. EFFECT OF THE CATALYST COMPOSITION

The effect of the catalyst composition on the performance has been studied from several aspects.

2.1. *Variable Cu content at fixed Pd*

The palladium content y was fixed at 5 and the Cu content x was varied in the range from 0 to 1000. Using 2 g of these catalysts, the reaction was continued for 1 hr at 140°C. The feeding rate of the gas was 5 ml/min for both hydrogen and oxygen, 10 ml/min for nitrogen, and 5 ml/hr for liquid benzene at the inlet. The result is illustrated in fig. 3. Consistent with the results of fig. 2, the yield of phenol increases steadily with increasing amount of copper in the catalyst. It should be emphasized that the Pd-alone catalyst has no catalytic activity.

2.2. *Variable y at fixed x*

By keeping the copper content constant ($x = 250$) the amount of palladium (y) was varied in the range from 1 to 100. The reaction was continued for 1 hr

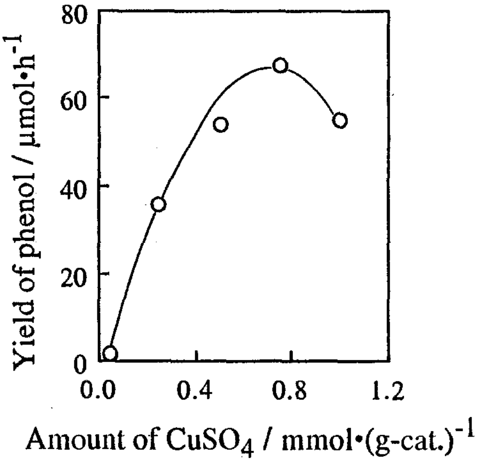

Fig. 3. Effect of Cu content in the catalyst. Catalyst: variable x-5 Pd, 2 g. Temp.: 140°C, Gas supply: Simultaneous (H_2, O_2: 5 ml/min, N_2: 10 ml/min, liq. benzene: 5 ml/h).

using 2 g of catalyst. The temperature was 140°C and the feeding gas was H_2: 5 ml/min; O_2: 5 ml/min; N_2: 10 ml/min; and liquid benzene: 5 ml/hr. The result is indicated in fig. 4, in which the turnover frequency calculated for palladium is also shown [9]. As is seen, the phenol yield makes a maximum at about $y = 25$–50 and the further increase in y tends to decrease the yield of phenol. On the other hand, the turnover frequency takes the highest value at the lowest y studied indicating that the profitable y value is a matter of choice.

3. *Effect of the rate of feeding gases*

In order to see the effect of partial pressure of each individual component, the flow rate of a given gas, say hydrogen, was varied and the variation of its

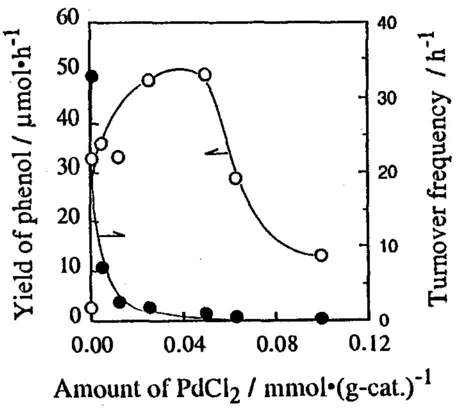

Fig. 4. Effect of Pd content in the catalyst. Catalyst: 250Cu-variable y; other conditions were the same as fig. 3. The turnover frequency was calculated for Pd.

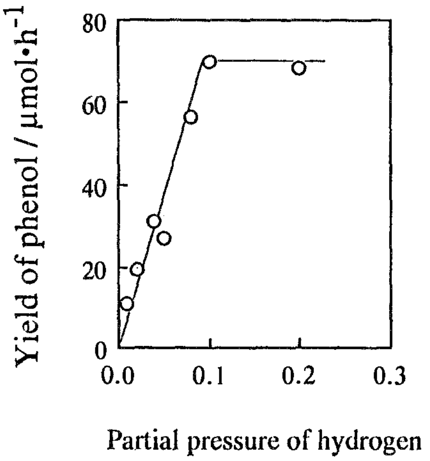

Fig. 5. Effect of the partial pressure (flow rate) of hydrogen in the reaction mixture.

flow rate was balanced by adjusting the rate of nitrogen for keeping the total gas rate constant (88 ml/min) [10].

Fig. 5 shows the effect of the partial pressure of hydrogen. To obtain this figure, the rates of benzene and oxygen were fixed at 36 and 4 ml/min, respectively, and the sum of the rates of hydrogen and nitrogen was fixed at 48 ml/min. The reaction temperature was 200°C. According to this figure, the yield of phenol is linearly dependent on the partial pressure of hydrogen when it is below 0.1. Similar studies were done for both oxygen and benzene separately. Regarding the partial pressure of benzene, the linear part extends up to $p = 0.4$ suggesting rather a lower reactivity of benzene. On the other hand, the linear part for oxygen exists in the narrower range of oxygen pressure, ca. 0.08 or less.

4. Conclusion

The present study revealed that an appreciable amount of phenol is produced only when the Pd-Cu composite catalyst is used indicating that the $Cu^{I/II}$ redox couple plays an essential role in the reaction. In contrast to the similar reaction in the liquid phase, the use of a Pd-single component catalyst is totally ineffective in the gas phase reaction. In addition, the yield of p-benzoquinone, which shares an appreciable part of the product selectivity in the liquid phase reaction, is minimized in the gaseous reaction. This is an additional advantage of doing the reaction in the gas phase.

Regarding the production rate, the best result here obtained is ca. 60 µmol/hr,g-SiO_2. In order to become a practical phenol producing process, further improvements in the catalyst activity are required. Studies along this line are in progress.

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[9] For figs. 2 and 3, the turnover frequency for palladium is given by dividing the number in the ordinate scale by 100. The rate of phenol production is rather slow and is ca. 60 μmol/hr, g-SiO_2 at best. This makes the turnover number calculated for copper very low in most data which were determined after 1 hr of reaction. In a prolonged reaction continued for 23 hours using a 750Cu-50Pd catalyst, the value became 1.24 indicating that the copper redox couple is certainly cycling.

[10] In this value, the rate of benzene is expressed in terms of the corresponding vapor rate at room temperature.